



Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number:

0 310 164
A1

⑫

EUROPEAN PATENT APPLICATION

⑬ Application number: 88202014.2

⑮ Int. Cl.4: C10G 47/02 , C10G 65/10 ,
B01J 21/04 , B01J 29/16

⑭ Date of filing: 14.09.88

⑯ Priority: 29.09.87 GB 8722840

⑰ Applicant: SHELL INTERNATIONALE
RESEARCH MAATSCHAPPIJ B.V.
Carel van Bylandtlaan 30
NL-2596 HR Den Haag(NL)

⑰ Date of publication of application:
05.04.89 Bulletin 89/14

⑰ Designated Contracting States:
BE DE FR GB IT NL SE

⑰ Inventor: Van Dijk, Nicolaas
Carel van Bylandtlaan 30
NL-2596 HR The Hague(NL)
Inventor: Esener, Aydin Ali
Badhuisweg 3
NL-1031 CM Amsterdam(NL)

⑰ Representative: Aalbers, Onno et al
P.O. Box 302
NL-2501 CH The Hague(NL)

⑯ Process for converting a hydrocarbonaceous feedstock.

⑯ Process for converting a hydrocarbonaceous feedstock into products of lower average boiling point by contacting the feedstock at elevated pressure and temperature with hydrogen over a bed of a catalyst A producing hydrocracked effluent and subsequently contacting at least part of said hydrocracked effluent with hydrogen over a bed of a catalyst B, whereby catalyst A comprises an amorphous cracking component, at least one metal of Group VIB and/or Group VIII of the Periodic Table of the Element and fluorine, and whereby catalyst B comprises a faujasite-type zeolite and at least one metal of Group VIB and/or Group VIII of the Periodic Table of the Elements.

EP 0 310 164 A1

PROCESS FOR CONVERTING A HYDROCARBONACEOUS FEEDSTOCK

The present invention relates to a process for converting a hydrocarbonaceous feedstock into products of lower average boiling point by contacting the feedstock with hydrogen over a series of beds of catalysts.

It is known to subject a heavy hydrocarbonaceous feedstock to a hydrocracking process which makes use of more than one bed of catalyst. US-A-4,211,634 describes a hydrocracking process by contacting a hydrocarbonaceous feedstock with hydrogen over a first zeolitic catalyst comprising nickel and tungsten or nickel and molybdenum, and contacting the resulting hydrocracked product with hydrogen over a second zeolitic catalyst containing cobalt and molybdenum. In EP-A-0,183,283 a hydrotreating process is described in which a residual oil is passed together with hydrogen over a stacked-bed catalyst, wherein said stacked-bed comprises an upper zone containing an amorphous cracking catalyst with a compound of a Group VIB and Group VIII metal and a phosphorus compound, and a lower zone containing a different amorphous cracking catalyst with a compound of a Group VIB and VIII metal and substantially without a phosphorus compound.

It is further known that fluoriding a hydrocarbon conversion catalyst can improve the suitability of such a catalyst in hydrocarbon conversion processes. The improved suitability is shown by a greater activity in the conversion of the heavy hydrocarbonaceous feedstock. In this respect reference is made to GB-A-1,545,828, describing a process for incorporating fluorine into an amorphous or zeolitic hydrocracking catalyst by contacting said catalyst with a fluorine-containing compound and using a constant or varying fluorine slip. The catalyst thus fluorided is capable of giving a higher yield of desired product at a lower temperature than a catalyst not fluorided that way.

It has now surprisingly been found that an unexpectedly high activity gain is obtained when in an operation employing a series of beds of catalysts a fluorided amorphous catalyst is used, a first bed containing the fluorided amorphous catalyst and a second bed containing a zeolitic catalyst. Accordingly, the present invention provides a process for converting a hydrocarbonaceous feedstock into products of lower average boiling point by contacting the feedstock at elevated pressure and temperature with hydrogen over a bed of a catalyst A producing a hydrocracked effluent and subsequently contacting at least part of said hydrocracked effluent with hydrogen over a bed of a catalyst B, whereby catalyst A comprises an amorphous cracking component, at least one metal of Group VIB and/or Group VIII of the Periodic Table of the Elements and fluorine, and whereby catalyst B comprises a faujasite-type zeolite and at least one metal of Group VIB and/or VIII of the Periodic Table of the Elements.

Catalyst A contains an amorphous cracking component. Suitable amorphous cracking components include refractory oxides, such as alumina, silica, silica-alumina, magnesia, titania, zirconia and clays. The use of alumina as amorphous cracking component is preferred.

The catalytically active metals on catalyst A are selected from Groups VIB and VIII of the Periodic Table of the Elements. Suitably these metals are molybdenum and/or tungsten, and/or cobalt and/or nickel, and/or palladium and/or platinum. When the catalytically active metals are non-noble, they are preferably present on catalyst A in their oxidic form and in particular in the form of their sulphides. Thereto, the catalyst can be (pre)sulphided, converting the metal oxides into metal sulphides. This can be achieved by using either H_2S as such or H_2S obtained by hydrogenation of organic sulphur compounds such as sulphur-containing oil fractions, as is known in the art.

To obtain the synergistic effect the catalyst A contains fluorine. Various ways to incorporate fluorine into catalysts are known in the art. In this respect reference is made by the above-mentioned GB-A-1,545,828, and further to US-A-4,598,059 and GB-B-2,024,642, all specifications describing the use of gaseous fluorine-containing compounds, such as 1,1-difluoroethane and ortho-fluorotoluene. Another way of preparing fluorine-containing amorphous catalysts is by impregnation, e.g. as described in GB-A-1,156,897. Other suitable methods include those described in US-A-3,673,108 and US-A-3,725,244.

The amounts of all components on catalyst A are not critical. Preferably the catalyst A comprises from 6 to 24 %w of at least one metal of Group VIB, from 1 to 16 %w of at least one metal of Group VIII and from 0.5 to 10 %w of fluorine, the weight percentages being based on total catalyst. During operation the amount of fluorine on the catalyst tends to decrease as fluorine compounds are detached from the catalyst and entrained by the streams of hydrogen and hydrocracked products. Therefore, it is preferred to add a fluorine-containing compound to the feedstock in order to maintain the fluorine content of catalyst A at the desired level.

In the first bed the feedstock is hydrocracked and organic nitrogen compounds and/or organic sulphur-containing compounds, if present therein, are converted into products with lower boiling points and NH_3 and

H_2S , respectively. The present invention includes processes in which the NH_3 and H_2S and optionally part of the light hydrocarbons are separated from the hydrocracked effluent. The separation can e.g. be effected by washing with water (to remove NH_3 and H_2S) and/or a distillation (to remove at least some hydrocarbons with a boiling point below e.g. 350 °C). However, preferably the process is carried out such that 5 substantially the whole hydrocracked effluent from the bed of catalyst A is contacted with hydrogen over the bed of catalyst B, i.e. without an intermediate separation or liquid recycle.

The process conditions prevailing in the bed of catalyst A are preferably a temperature of from 280 to 450 °C, a hydrogen (partial) pressure of from 25 to 200 bar, a space velocity of from 0.3 to 5 kg/l.h and a hydrogen to feedstock ratio of from 100 to 3000 Nl/kg.

10 It is remarked that when the present process is carried out such that substantially the whole hydrocracked effluent from the bed of catalyst A is passed over the bed of catalyst B the hydrocracked effluent may contain fluorine compounds. These fluorine compounds may incur incorporation of fluorine into catalyst B.

15 Hence the present invention also covers processes using a bed of catalyst A and a bed of catalyst B wherein not only catalyst A but also catalyst B contains fluorine. Conveniently catalyst B used in the present process further comprises fluorine. The preferred amount of fluorine in catalyst B ranges from 0.5 to 10 %w, based on the total catalyst.

20 Fluorine may be applied on catalyst B during the operation or before the catalyst B is used in the hydroconversion process of the present invention. So it is possible to start the process with a bed of fluorinecontaining catalyst A and a bed of fluorine-free catalyst B. During operation some of the fluorine from catalyst A detaches from the catalyst and may be contacted with catalyst B together with (part of) the hydrocracked effluent, thereby partly attaching to catalyst B. In the state of the art several methods are 25 known to prepare fluorine-containing zeolites. Suitable methods include those described in the above-mentioned GB-A-1,545,828, and US-A-4,598,059. Further suitable methods are described in US-A-3,575,887 and US-A-3,702,312. The amount of fluorine on catalyst A may be kept constant, e.g. by supplying a fluorine compound via the feedstock.

30 Catalyst B comprises a faujasite-type zeolite. Such a zeolite includes naturally occurring faujasite, synthetic zeolite X and synthetic zeolite Y. Preferably the faujasite-type zeolite is zeolite Y. The zeolite Y is characterized by the faujasite X-ray diffraction pattern and suitably has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 4 to 25, in particular from 6 to 15. The unit cell size of Y zeolites preferably ranges from 2.420 to 2.475 nm. Suitably 35 the zeolite Y is one as described in European patent applicaton No. 87200919.6 or in European patent application No. 87200920.4 (Applicants reference T 5011 and T 5012, respectively). Such zeolites are characterized by a unit cell size below 2.440 nm, preferably below 2.435 nm, a degree of crystallinity which is at least retained at increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios, a water adsorption capacity (at 25 °C and a 40 p/p_0 value of 0.2) of at least 8% by weight of zeolite and a pore volume of at least 0.25 ml/g wherein between 10% and 60% of the total pore volume is made up of pores having a diameter of at least 8 nm (p/p_0 stands for the ratio of the partial water pressure in the apparatus in which the water adsorption capacity is determined and the saturation pressure of water at 25 °C).

40 More preferably zeolites are used wherein between 10% and 40% of the total pore volume is made up of pores having a diameter of at least 8 nm. The pore diameter distribution is determined by the method described by E.P. Barrett, G. Joyner and P.P. Halenda (J. Am. Chem. Soc. 73, 373 (1951) and is based on the numerical analysis of the nitrogen desorption isotherm. It should be noted that inter-crystalline voids are excluded in the determination of the percentage of the total pore volume made up in pores having a diameter of at least 8 nm when said percentage is between 10% and 40%.

45 Apart from the faujasite-type zeolite, catalyst B preferably also comprises an amorphous refractory oxide. Suitable amorphous oxides include silica, alumina, silica-alumina, thoria, zirconia, titania, magnesia and mixtures of two or more thereof. The refractory oxides may be used as binder and/or as an amorphous cracking component. It is advantageous to use alumina as amorphous cracking component which also acts as binder. The amount of refractory oxide may suitably vary from 10 to 90 %w based on the total of 50 refractory oxide and faujasite-type zeolite.

55 Catalyst B comprises at least one metal of Group VIB and/or Group VIII of the Periodic Table of the Elements. Preferably catalyst B comprises one or more nickel and/or cobalt compounds and one or more molybdenum and/or tungsten compounds and/or one or more platinum and/or palladium compounds. The metal compounds in catalyst B are preferably in the oxidic and/or sulphidic form. The metal compounds are more preferably in sulphidic form. Conveniently, the catalyst has been subjected to a sulphiding treatment prior to actual use in a hydrocracking process.

Preparation of metals-containing catalyst B is known in the art. Preparation methods include impregnation, ion exchange, and co-mulling of the ingredients.

The amounts of metal compounds in catalyst B may suitably range from 2 to 20 parts by weight (pbw) of one or more Group VIB metals and from 1 to 10 pbw of one or more Group VIII metals, calculated as m tal per 100 pbw of the total of faujasite-type zeolite, metal compounds and refractory oxide, if present. For platinum and/or palladium compounds the amount is suitably from 0.2 to 2 pbw per 100 pbw of total of 5 zeolite, metal compounds and refractory oxide, if present.

The process conditions prevailing in the bed of catalyst B can be the same or different from these prevailing in the bed of catalyst A and are suitably selected from a temperature from 280 to 450 °C, a hydrogen (partial) pressure from 25 to 200 bar, space velocity from 0.3 to 5 kg/l.h, and a gas/feedstock ratio from 100 to 3000 Nl/kg.

10 It is evident that the beds with catalysts A and B, respectively, can be constituted of one or more beds of catalyst A and one or more beds of catalyst B. And it is also evident that the bed or beds with catalyst A and the bed or beds with catalyst B can be located in one or more reactors. The ratio of the volume of the bed of catalyst A to that of the bed of catalyst B can be varied within wide ranges and may preferably be selected from the range 1:5 to 10:1. It is evident that the bed of catalyst B may be followed by another bed 15 of catalyst A which may be followed by a bed of catalyst B and so on. The advantageous activity gain is already obtained after one sequence of one bed of catalyst A and one of catalyst B.

16 Hydrocarbonaceous feedstocks that can be used in the present process include gas oils, vacuum gas oils, deasphalted oils, long residues, short residues, catalytically cracked cycle oils, thermally cracked gas oils and syncrudes, optionally originating from tar sands, shale oils, residue upgrading processes or 20 biomass.

25 Combinations of various hydrocarbonaceous feedstock can also be employed. The hydrocarbonaceous feedstock will generally be such that a major part, say over 50 %wt, has a boiling point above 370 °C. The present process is most advantageous when the feedstock contains nitrogen. Typical nitrogen contents start from 50 ppmw. The feedstock will generally also comprise sulphur compounds. The sulphur content will usually be in the range from 0.2 to 6 %wt.

The invention will be further illustrated by means of the following Example.

EXAMPLE

30

Four catalyst systems are compared in 4 tests. In all tests a Middle East flashed distillate feedstock is used of which 95 %w has a boiling point of at least 370 °C (370 °C), and a nitrogen content of 1100 ppmw. In the tests three catalysts are investigated: catalyst A being a commercial hydroconversion catalyst comprising 13.0 %w Mo, 3.0 %w Ni and 3.2 %w P on alumina, catalyst A' being like catalyst A but 35 containing in addition 3 %w F, and catalyst B being a zeolitic catalyst comprising 7.7 %w W and 2.3 %w Ni. The carrier of catalyst B consists of 25 %w alumina and 75 %w zeolite Y, the zeolite Y having a unit cell size of about 2.451 nm. During the tests the following conditions are applied: a temperature of 375 °C, a hydrogen pressure of 90 bar, an overall space velocity of 0.5 kg/l.catalyst.h and a gas/oil ratio of 1500 Nl/Kg. The total amount of catalyst used is the same in all tests, but in tests 1 and 3 the catalyst consists of 40 catalyst A and A', respectively, whereas in tests 2 and 4 the total amount of catalyst is divided into a first bed of catalyst A or A', amounting to half the total amount, and a second bed of catalyst B, also amounting to half the total amount. During the latter tests no liquid recycle or intermediate separation between the two catalyst beds occurs. Further conditions and results of the tests are indicated in the following Table.

45

TABLE

Test No.	1	2	3	4
Catalyst system	A	A+B	A'	A'+B
370 °C-fraction in product, %w on feed	73.4	73.4	64.9	57.5

50 From the comparison of the results of tests 1 and 3 it is apparent that the conversion of 370 °C material is increased if a fluorine-containing catalyst is used. Comparison of the results of tests 1 and 2 teaches that the conversion of 370 °C material is the same in these tests. Hence, it would be expected that in test 4 about half the improvement as obtained in test 3, would be attained. It is therefore very surprising that the conversion of the heavy hydrocarbons in test 4 is far better than the conversion obtained in test 3.

Claims

1. Process for converting a hydrocarbonaceous feedstock into products of lower average boiling point by contacting the feedstock at elevated pressure and temperature with hydrogen over a bed of a catalyst A producing hydrocracked effluent and subsequently contacting at least part of said hydrocracked effluent with hydrogen over a bed of a catalyst B, whereby catalyst A comprises an amorphous cracking component, at least one metal of Group VIB and/or Group VIII of the Periodic Table of the Element and fluorine, and whereby catalyst B comprises a faujasite-type zeolite and at least one metal of Group VIB and/or Group VIII of the Periodic Table of the Elements.
- 10 2. Process according to claim 1, in which the amorphous cracking component is alumina.
3. Process according to claim 1 or 2, in which catalyst A comprises molybdenum and/or tungsten and/or cobalt and/or nickel and/or platinum and/or palladium.
4. Process according to any one of claims 1 to 3, in which catalyst A comprises from 6 to 24 %w of at least one metal of Group VIB, from 1 to 16 %w of at least one metal of Group VIII and from 0.5 to 10 %w of fluorine, the weight percentages being based on total catalyst.
- 15 5. Process according to any one of claims 1 to 4, in which the process conditions prevailing in the bed of catalyst A are a temperature of from 280 to 450 °C, a hydrogen (partial) pressure of from 25 to 200 bar, a space velocity of from 0.3 to 5 kg/l.h and a hydrogen/feedstock ratio of from 100 to 3000 Nl/kg.
6. Process according to any one of claims 1 to 5, in which catalyst B further comprises fluorine.
- 20 7. Process according to claim 6, in which catalyst B comprises from 0.5 to 10 %w of fluorine.
8. Process according to any one of claims 1 to 7, in which the faujasite-type zeolite of catalyst B is zeolite Y.
9. Process according to any one of claims 1 to 8 in which catalyst B contains one or more nickel and/or cobalt compounds and one or more tungsten and/or molybdenum compounds; and/or one or more platinum and/or palladium compounds.
- 25 10. Process according to any one of claims 1 to 9, in which the following conditions prevail in the bed of catalyst B: a temperature from 280 to 450 °C, a hydrogen (partial) pressure from 25 to 200 bar, a space velocity of 0.3 to 5 kg/l.h, and a gas/feedstock ratio of 100 to 3000 Nl/kg.

30

35

40

45

50

55



EP 88202014.2

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	US - A - 3 891 539 (NELSON) * Claims * --	1-5, 9, 10	C 10 G 47/02 C 10 G 65/10
A	US - A - 3 853 742 (WARD) * Claims * --	1, 2, 8- 10	B 01 J 21/04 B 01 J 29/16
A	US - A - 3 730 878 (POLLITZER) * Claims; abstract * --	1-4, 8, 9	
D, A	US - A - 4 211 634 (BERTOLACINI) * Claims * --	1, 9, 10	
D, A	US - A - 3 725 244 (SCHUTT) * Claims * -----	1, 6, 7, 9	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 10 G B 01 J C 07 C 4/00
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
VIENNA	03-01-1989	BECKER	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone			
Y : particularly relevant if combined with another document of the same category			
A : technological background			
O : non-written disclosure			
P : intermediate document			